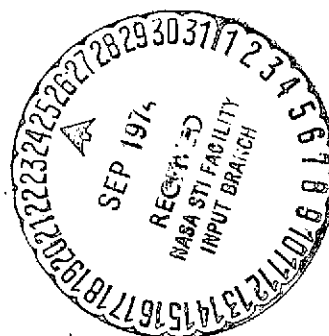


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16. Abstract The use of electron microscopy in soil study research was studied with respect to general preparatory methods, specific preparatory methods and the problems of evaluating pictures. The method of ultrasonic disintegration was developed and used, and descriptions of some structural observations which aid in the identification of major soil components are presented.			
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OUR EXPERIENCES IN THE POSSIBLE USE OF THE ELECTRON
MICROSCOPE IN SOIL STUDY EXPERIMENTS

G. Pártay

The electron microscope and its field of science is still /389*
relatively young -- a child of this century. The preparatory
research started at the beginning of the century, and the first
usable electron microscope appeared in the thirties.

In our country, the research started in 1952 at the Hungarian
Academy of Science Central Electron Microscope Laboratory, and,
starting in the early sixties, branched out to a variety of
specialized fields of science.

The general electron optical and preparatory information
(special nomenclature and explanation of concepts, etc.) is avail-
able in a number of well-written domestic and foreign handbooks
and other publications [1, 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 14,
15, 17, 19, 20]. We do not wish to deal with these, but would
like to publish our experiences relating to soil study experiments.
We have to emphasize that in the following the characteristics of
minerals are examined from the point of view of electron microscopy.
Thus, when we refer to a picture as definable or nondefinable, it
does not mean that we are referring to other methods or instru-
ments as well. It is true that for structure determination it is
necessary to consider information from a variety of instruments
and experiments. There are, however, two methods in which one has
to totally rely on the electron microscope; these are selective
microdiffraction and submicroscopic particle measurements.

* Numbers in the margin indicate pagination in the foreign text.

General Preparatory Conditions

In each case our instrument was the Tesla BS 242A type electron microscope, which has a final magnification of 35,000x, a resolution of 40 Å, and an accelerating voltage of 40 kV. Our photography was done on Orwo slides and Agfa Agepe FF film. In order to get pictures which it is possible to evaluate, a few special demands must be met: acceptable dispersion, layer thickness (transparency), particle size, the prevention of byproduct formation, and, if necessary, increasing the contrast.

In soil study practice, one uses the Kachinsky method for the preparation of suitable particle size fractions for physical and chemical analyses, the Gorbunov or Jackson method of preparation for X-ray examinations, and similar methods for thermal analyses. At first, as a general method, we dispersed the sample in 0.01 N NH_4OH solution in an agate mortar. Grinding in the motor with the ammonia medium acting as detergent is intended to prevent coagulation in the sample preparation. However, we found that this method, which was developed for the preparation of pure clay minerals, is not always applicable to soils. In soil we find, even from a preparatory point of view, a complex system of matter, the components of which resist these dispersion experiments. Here we mean the salt and organics content, the amorphous materials, the biological and chemical binding of the particles. In order to improve our results, we tried to find another medium to increase the degree of dispersion, for example, colloid-solution, washed quartz, etc. These experiments were unsuccessful, especially since the need arose for a preparatory technique which would satisfy the demands of all three analytical methods (electron microscopy, X-ray, DTA-DTG), would give results that are easily evaluated and reproducible, is fast, makes it possible to approach a problem from several aspects, creates few subjective error possibilities, and does not form byproducts.

This is necessary on the one hand for the examination of characteristics, and, on the other, for the electron microscope's /390
photographic technique, because there is a connection between the contrast, the layer thickness and the applied accelerating voltage. The greater the applied voltage, the greater the transparent layer thickness, and the lower the resolution. The recognition of this fact among others made the development of low voltage electron microscopy possible in the last decade. The use of a 50-kV accelerating voltage permits the examination of approximately a 0.1 μm layer thickness. Due to the great depth of focus, every structure in this thickness is photographed. Thus, one has to be very careful when evaluating the pictures.

First we experimented with a vibrator method. We weighed 0.5 g material into 50 ml 0.10 N NH_4OH and shook it for 24-25 hours, taking samples for examination immediately after shaking as well as after settling for 1, 24 and 48 hours. These experiments gave considerably better results than the grinding method. Although we got enough identically prepared material to be examined in all the instruments, the preparation took much too long. Thus, the purpose of the following experiments was to shorten the time involved. In biological preparations, the use of a blender is a well-known technique. We weighed 4 g material into 0.01 N NH_4OH and blenderized it for 1, 2, 3 and 4 min. We took samples immediately as well as after 1, 24 and 48 hours settling. This took a satisfactorily short time, the degree of dispersion was high and no byproducts were formed. However, the basic disadvantages in all the preceding methods was that they required the use of a detergent and were material-specific and selective in soil studies. The montmorillonite series shown after 2-min treatment (Fig. 1) and after 4-min treatment (Fig. 2) indicates that this method is not satisfactory. The members of this series are:

1. Veszprém montmorillonite
2. Istenmezeje bentonite

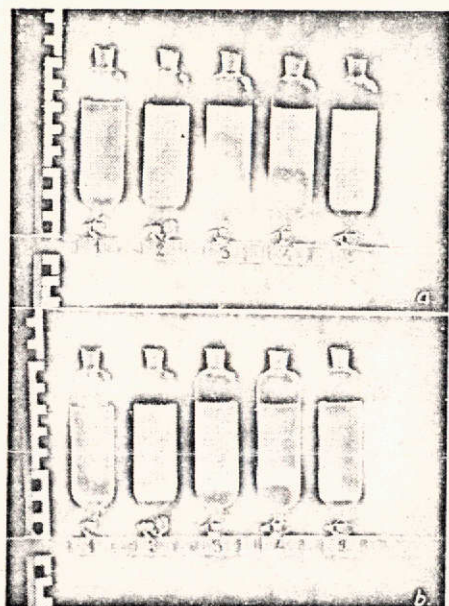


Fig. 1. Five different montmorillonites after 2 min of blenderizing: a) immediately after workup; b) after 48 hours settling.

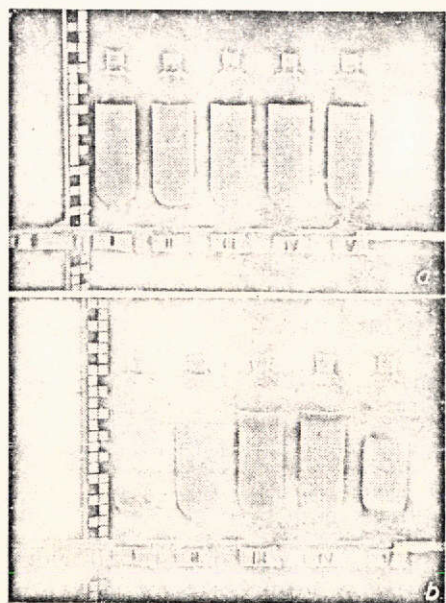


Fig. 2. Five different montmorillonites after 4 min of blenderizing: a) immediately after workup; b. after 48 hours settling

3. Kolduu spotted bentonite
4. Kolduu green bentonite
5. Istenmezeje bentonite (from a different assay)

Even the two Istenmezeje bentonites (2, 5) behave differently at the work-up. We could not achieve the ideal situation, where our suspension would not contain some large conglomerate particles. To this end, we introduced the ultrasonic technique, which satisfied all the demands mentioned above.

We have previously published [16] experiments related to the use of ultrasonic waves, background literature and part of our results.

The ultrasonic technique facilitates the fast, objective preparation of well-homogenized suspensions in water without the use of a detergent. The sample is then transferred to the membrane in the form of a microdroplet.

Special Preparatory Conditions

Attention should be called to a few problems. First of all, the behavior of the microdrop and the suspension is influenced by the surface tension characteristics of the membrane. On a nonhydrophilic membrane,

/391

the material suspended in the droplet will be deposited as a margin when the drop dries. In Fig. 3 we see a section from a sample of Szology dust precipitated around the edge of the droplet. Its composition cannot be determined. From Fig. 4, however, which comes from a depth of 0-1 cm in section I of Ökörü Lake (carbonated lake silt), we got more information due to better preparation.

The whole picture surface is covered by a very thin,

amorphous-appearing layer from which the illite platelets stand out like tiny islands. The largest particle is quartz, on which the recrystallized salts settle. The picture is enriched by a few other crystal formations, such as what appears to be amorphous SiO_2 as tiny but very electron-dense globular material and some other unidentifiable formations. The concentration in the margins can cause serious errors, partly because particles deposited on top of each other are useless for the purpose of morphological examinations, and partly because, not being visible, the observed selection is erroneous.

Furthermore, due to this conglomerate formation, performance of a selective microdiffraction also becomes impossible. In order to achieve our purpose, we experimented with a variety of membranes: cellulose acetate,

formvar, and carbon, as well as different wetting agents and procedures, e.g. NaOH, detergents, colloid suspensions and the use of ion bombardment. We tried to form a colloid suspension with our material, transfer this suspension to the membrane and

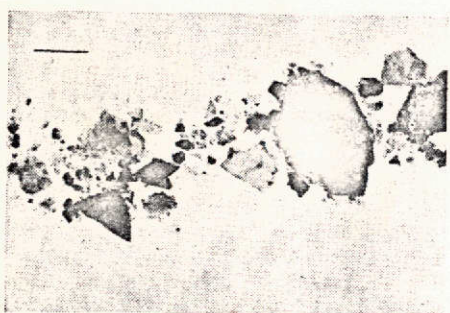


Fig. 3. Szology dust. Drop margin. Not shaded.

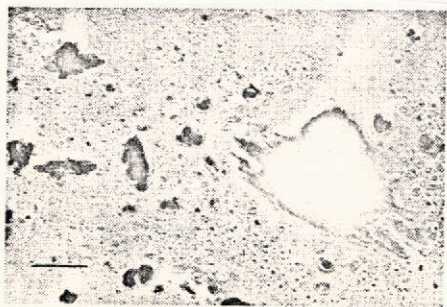


Fig. 4. Ökörü Lake section I. 0-1 cm, shaded with palladium.

precipitate it out of the colloid. In this way, the particles retain their position from the colloid.

This method is clumsy and requires a special membrane (silicon), because the generally used membranes dissolve or shrink from the colloid solvents. According to our observations, the best surface tension-diminishing effect was shown by the ion-bombarded carbon membrane. Less sensitive suspension with favorable physical-chemical characteristics (e.g. pure clay minerals) could be transferred to a formwar membrane directly after ultrasonic disintegration without further treatment.

After transferring the suspension to the membrane and drying it, it is sometimes necessary to shade it for the purpose of increasing the contrast and facilitating particle size measurement. This is done in vacuum by evaporating a metal which does not give a structure of its own. Such metals are: gold, aluminum, palladium, platinum or some combination of the above. In our experiments we use four-nine purity palladium, and, in each case, we shade at an angle of 20° . There is a known relationship between the height of the particle, the length of the shadow and the tangent of the shading angle. This way, we get information about our measured material in the third dimension as well. This relationship, however, only holds for strictly planar surfaces. In reality, there is no such thing, because the membrane hangs in between the openings of the microgrid; thus a correction factor has to be used.

/392

Another cause of error is that a semishadow is formed due to technical problems. Measurements and calculations show that on the average this is not more than 6%; therefore, 6% has to be subtracted from the length of the shadow.

Until the scanning method was developed, the transmission technique had to be used to determine what kind of surface the

material has. The reproduction procedure was suitable for the examination of the material's surface. We made a pasty suspension by grinding in a mortar for 10 min with 0.1 N NH_4OH . We transferred this to a slide and dried it. Then we tried to make a colloid or formwar copy of the surface. However, this was not always successful, since the poured colloid or formwar was absorbed by the material. Even if we succeeded in pulling off the film, it was full of small particles which were impossible to remove, thus forming a pseudo-reproduction. Another problem was that, due to the heterogeneous surface, the reproduction was torn and full of holes and could not be evaluated. Therefore, after the example of blood smears, we proceeded to make a smear from a suitably diluted suspension. With this method, we created not only technically favorable conditions, but we also achieved a certain amount of orientation of the particles, which, in this procedure, improves the evaluation. We made a carbon reproduction of this smear. This reproduction gave a very nice picture, rich in detail.

The photography in this case agrees with general electron microscope methods. However, we want to point out the danger represented by the selectiveness in the photography. This micro-grid, on which the material is placed, is a 3- or, sometimes, 2.3-mm diameter disc with approximately 40 usable holes representing a total area of 4 mm^2 . The area of a field of view at a magnification of 10,000x is $25 \mu\text{m}^2$, which means that if we want to see the total available area, we have to examine and photograph 160 sections. At higher magnification, of course, the situation is even less favorable. It becomes obvious from the data that, in soil study experiments, one has to proceed with circumspection. The careful and correct selection of a preparatory method is very important for the best possible use of the information contained in the sample. Another problem crops up with respect to particle size measurement. In the situation described above, a

5 μm or larger particle will not be in the field of view, or, rather, it will cover it completely. Therefore, the degree of magnification has to be selected very carefully, because, otherwise, we might distort the particle distribution function; however, one must not stray into optical microscopy magnitudes. In our experiments we examine 50 sections per microgrid and take 30 pictures per sample. It has been proven that this method is adequate for the study of the general mineral characteristics of soil sections. We select a degree of magnification between 5000x and 10,000x, and, after adequate preparation, we get well distributed, transparent and identifiable pictures. If we are doing an individual rather than a statistical examination, this method is not satisfactory: instead, we can achieve good results by a systematic examination of section after section.

Evaluation

There are several ways to evaluate and identify electron microscope pictures. The separation of clay mineral types can be done with the aid of atlases in the literature [2, 18]. These contain the typical pictures. However, it is not always possible to use these published pictures, since we only rarely find perfect particles in soil. They are partly in various phases of growth and partly the varying forms of breaks and erosions. These factors have to be considered when interpreting the pictures. Another possible way is to take a series of pictures of minerals originating in a variety of places and use these as standards of comparison. The advantage of this method is that it contains a statistical distribution of variables occurring in soil. With a large number of pictures it gives a very good basis for comparison in the identification of structures found in soil. In our laboratory, we used the latter method successfully in the examination of general mineral characteristics. However, the question comes up whether it would be possible to find stamps, identifying

/393

marks, which would enable the identification even in the absence of a characteristic morphological picture.

In the following, we list some examples to illustrate the possibilities of identification.

The kaolinite shows the well-known pseudohexagonal shape (Figs. 5 a and b). However, the crystal platelets often elongate in the (100) or (010) direction. If this elongation is large enough, we see a parallelogram-shaped figure with an elongated point, which could easily be mistaken for cerussite. It is very apt to coalesce, thus losing its classic shape and becoming unidentifiable. It also breaks easily, and the broken fragments are very difficult to recognize (Fig. 5 c). Taking the above into consideration, kaolinite is one of the most difficult minerals to identify by electron microscopy. Identification is only possible after very careful preparation and persistent examination, and then only on whole particles.

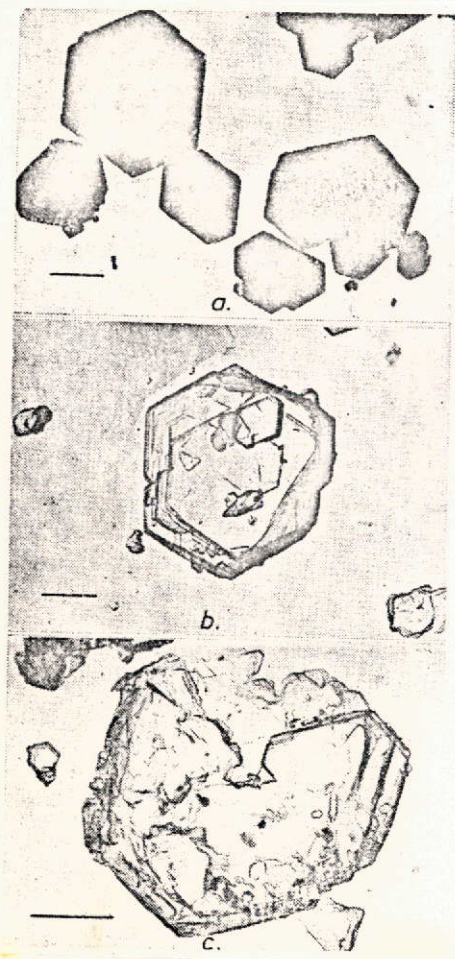


Fig. 5. Kaolinite.
a) Not shaded, b) and
c) carbon reproduction.

The rolled-up needles of the halloysite crystal plates (Fig. 6) are easily recognizable. In their determination, however, one always has to look for the periodic density increase and decrease which appears parallel to the lengthwise edge. This, /394 depending on the size of the crystal

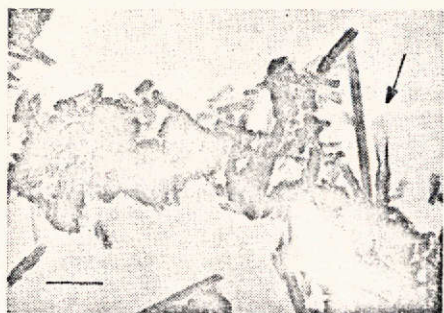


Fig. 6. Halloysite. The arrow points at a not-completely rolled-up crystal plate. Not shaded.

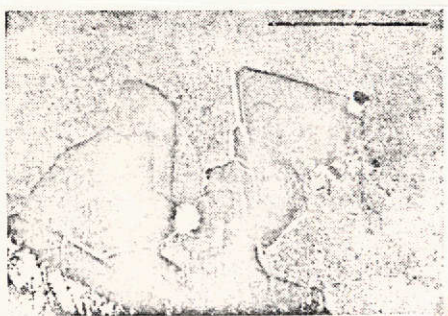


Fig. 7. Illite. Shaded with palladium.

plate, may occur once or several times with a distance of approximately 200 Å. It is necessary to note these characteristics in order to differentiate it from other minerals showing a similar picture but without this inner structure.

Illite appears in the form of a triangle with a rounded point (Fig. 7). It is frequently found in our soils. If, in soil studies, we find in our viewing field a multitude of 0.1 μ m scalelike configurations, it is most likely illite. However, the characteristic shapes have to be present, even though illite crystal plates from mined samples are often no larger than 1-1.5 μ m. Our experience is that they disperse very well; we never find aggregates as we do with kaolinite.

Muscovite (Fig. 8 a and b), from the point of view of determination, is also a rather problematic mineral, in spite of the fact that its large crystal plates are well oriented and translucent. These are characteristics of all the members of the mica group. However, we found that during electron microscopy, in muscovite a specific inner structure becomes visible, which resembles the moirè-error site diffraction. Presumably, in the muscovite crystal lattice, this represents the potassium error sites. We experimented with filling in or rearranging these error sites, but, for the time being, we could not prove our hypothesis. In any case, with the aid of this diffraction picture,

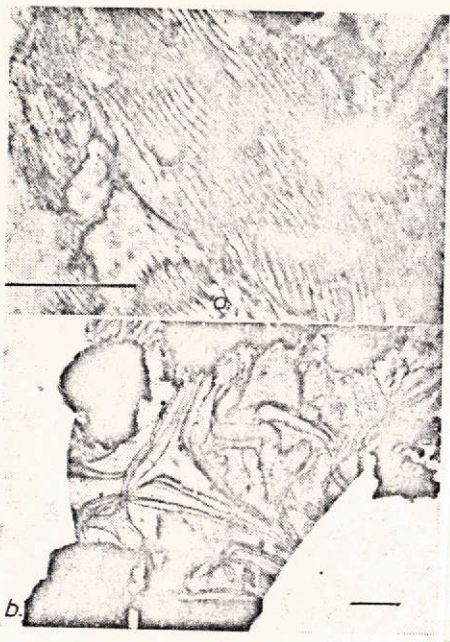


Fig. 8. Muscovite.
a) higher b) lower de-
gree of magnification.
Not shaded.

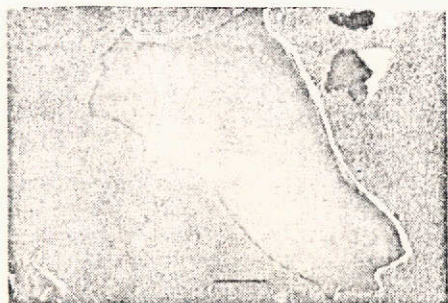


Fig. 9. Vermiculite.
Shaded with palladium.

we could identify muscovite very well. We find somewhat similar structural pictures with a few other minerals as well (e.g., pyrophyllite, chlorite), but they are quite different and cannot be confused with muscovite. In our opinion, this method of identification is also important with minerals (e.g., vermiculite, Fig. 9) that appear identical to muscovite, but do not show this inner structure.

Montmorillonite is greatly responsible for the physical and chemical condition of soil. It tends to appear as one of two main types. One of them is an irregular polygonal plate, which is very thin and has a magnitude of 1-2 μm , with slightly curling edges. It gives a very characteristic, unmistakable picture (Fig. 10 a and b). In Fig. 10 c, d, we marked with arrows those points which serve as a basis for identification of montmorillonite in soil pictures. The other type is a conglomerate of tiny 0.1 μm scales, which are easily confused with

similar-appearing amorphous materials found in soil. In this case, one cannot make a positive identification, and further examination is necessary. The reproduction method is not acceptable here, because materials always present in soil will precipitate out in the dried sample and might completely cover up the thin crystal plates of the montmorillonite (Fig. 11).

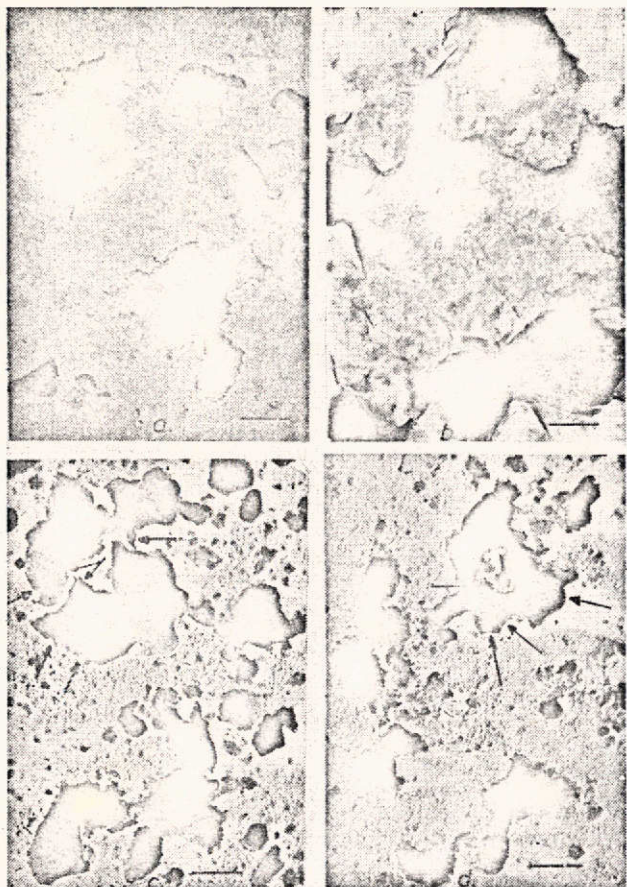


Fig. 10. a) Veszprém montmorillonite.
b) Koldu green bentonite; c) Újfőhér section 4, 28-42 cm;
d) 43-56 cm. Shaded with palladium.



Fig. 11. Montmorillonite.
Carbon reproduction.

The very electro-dense quartz particles are also highly characteristic (Fig. 12); they are predominant even in the preparation made from the sediment fraction. Its reproduction shows a characteristic cracked shell surface. In this case, however, the reproduction method is very useful, and provides a great deal of information. In the examination of soils, one of the important problems is the crystalline or amorphous state of the quartz, or, rather, the quantitative ratio of the two phases. This ratio can be determined with electron diffraction, but only

if the instrument's physical characteristics, stability and optical system satisfy the requirements of the Bragg equation.

We have listed here the characteristics of a few mineral types which occur most frequently in soil. Naturally, not only these constitute soil, but the examination

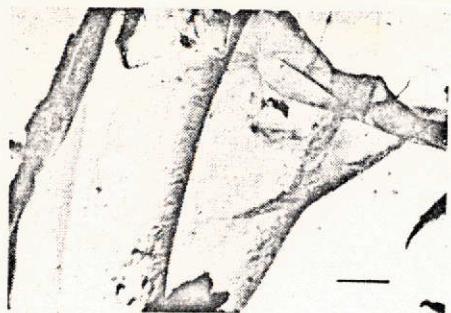


Fig. 12. Quartz. Carbon reproduction.

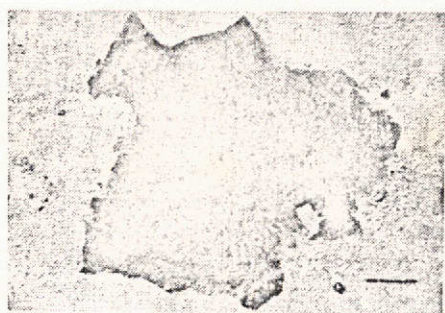


Fig. 13. Sample from Besenyszög 22 soil section. Meadow soil, 90-110 cm.



Fig. 14. Sample from the Apaj 3 soil section. Crusty meadow soil, 11-26 cm.

of the other components is difficult since they are dispersed in low quantities. These problems were discussed in the preparatory section. The use of the electron microscope for routine examinations of this nature is not recommended either from a scientific or economic point of view.

In addition to achieving homogeneous and well dispersed samples, the ultrasonic method is particularly useful in electron microscopy because of its liberating effect due to cavities. As a result, we could observe degradation phenomena in individual crystals. On the photographs (Figs. 13 and 14), one can see the thinning areas as well, and from these it can be determined that the erosion does not occur evenly from all sides; there are sections more resistant to crumbling. We could not study this phenomenon further because our instrument did not have the required resolution and magnification. Byproduct formation cannot be considered at this energy level and duration; we provided this empirically on another occasion [16].

In any case, this is a special field of application for the electron microscope which is very helpful in the understanding of process occurring in soil.

With electron microscope soil analysis one can also determine other objectives in addition to the identification of mineral components.

We developed a modification of the vibrator method and used it successfully for the determination of organic matter and microflora in rendsina soils. We shook 2 g of material in 100 ml 0.01N NH_4OH for 0.5 and 5 hours. Samples were taken immediately, as well as after 2 hours settling, and, in order to increase the contrast, they were treated with 1% phosphotungstic acid. Our results were published in a previous paper [21] (Fig. 15). We

find diatoms in many cases which supports our belief that the soil, from which our sample came, represents an area that was once under water for a long time. In a few samples, we succeeded in finding amorphous SiO_2 globules; this observation agrees completely with Iler's [11] experiments (Fig. 17).

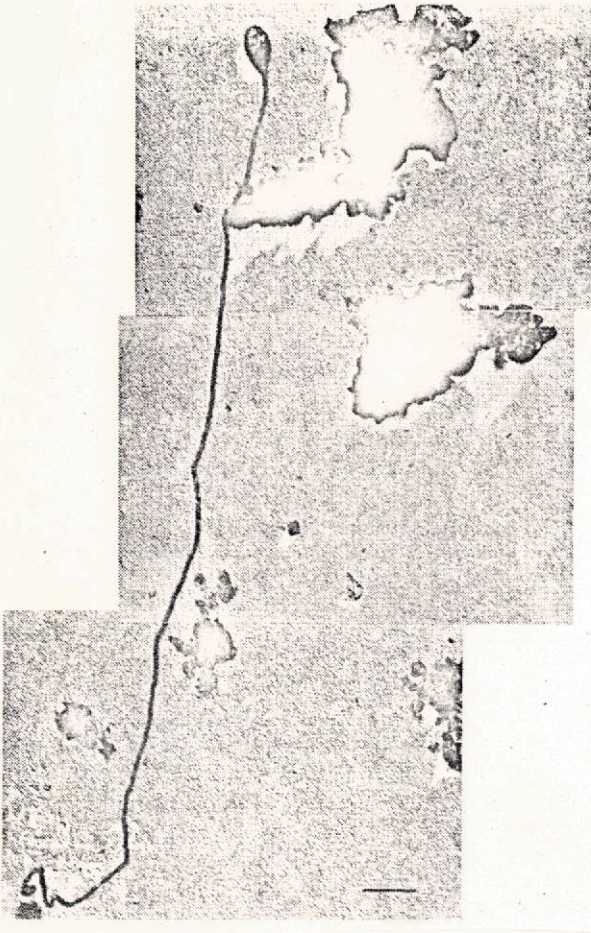


Fig. 15. Submicroscopic picture from rendsina soil. Shaded with palladium. Montage.

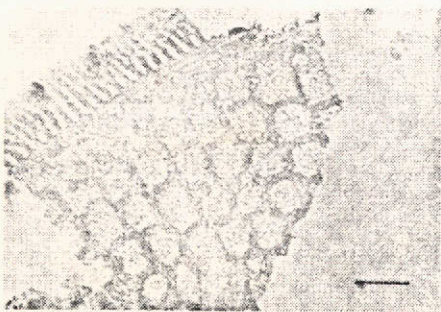


Fig. 16. Diatomaceous earth.

Summary

We experimented with the use of transmission electron microscopy in soil research with special consideration to the study of the methods and problems of

- 1) general preparation
- 2) specific preparation
- 3) picture evaluation.

We developed and used the ultrasonic disintegration as a general and, in some cases, specific preparatory method. For rendsina soils, we used post-contrasting with phosphotungstic acid. In the examination of mineral characteristics, we noted

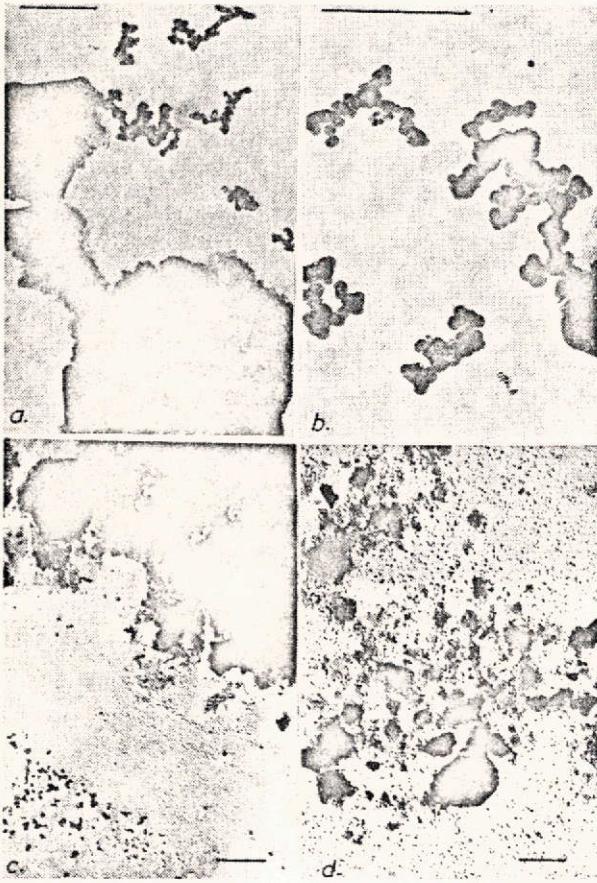


Fig. 17. a) Ocean silt. b) Section from a). c) Újfehér lake section 4, 56-70 cm. d) Conglomerate from the surroundings of Fertőboz section 1.

those structural stamps which aid in the identification of the major components of soil samples.

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